Supplementary information

Polymer Solar cells based on D-A Low Bandgap Copolymers Containing Fluorinated Side Chains of Thiadiazoloquinoxaline Acceptor and Benzodithiophene Donor Units

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1.0 Experimental section

1.1. General characterization methods

1.2. Synthesis

All the chemical reagents were obtained from Sigma-Aldrich. Toluene was freshly dried over sodium and benzophenone prior to use. Monomers M1 [1], M2 [2], M3 [3], and M4 [4] were synthesized according to previously reported procedures.

Polymer P0F: Monomer **M1** (0.6738g, 0.5mmol) and monomer **M4** (0.4523g, 0.5mmol) were added into a 25 mL flask equipped with a condenser under argon atmosphere.16mL toluene was added the mixture was degassed for 30min followed by addition of $Pd(Ph_3P)_4$(0.027g, 0.040mmol in dry box. Solution was heated at 110˚C for 48h.Then cooling to room temperaturepolymer solution was poured into vigorously stirred into methanol. Next obtained polymer was purified by Soxlet extraction using methanol, hexane to remove oligomer and small molecular part, and finally extracted with chloroform. The chloroform solution was then concentrated and precipitated in methanol. Dark colored solid was collected and dried under vacuum 20h. P0F(yield:0.71g, 81%). ^{1}H NMR(400MHz,$CDCl_3$):10.00-6.800(br, 20H,Ar), 3.12 (br, 4H,CH_2-Thiophen), 0.25-2.12 (br, 130H,Alk). Anal. Calcd for $C_{116}H_{154}N_4S_5$,%: C,78.95; H, 8.80; N,3.17; S, 9.08. Found, %: C, 78.56; H,8.56; N,3.00;S, 8.68.

Polymer P2F was prepared by similar way. (yield: 0.70g, 78%).^{1}H NMR (400 MHz,$CDCl_3$) δ: 10.20-6.80(br,18H, Ar), 3.13 (br, 4H, CH_2-Thiophen), 2.25-0.25 (br,128 H). ^{19}F NMR

($CDCl_3$) δ:-113.44 (s). Anal. Calcd for $C_{116}H_{152}F_2N_4S_5$,%: C,77.37; H, 8.51; N,3.11; F,2.11;S,8.90.Found,%: C,77.06; H,8.37; N,2.98; F,1.84;S, 8.63.

Polymer P4F was prepared by similar way. (yield: 0.65g, 71%).^{1}H NMR(400MHz, $CDCl_3$) δ: 10.10-6.50(br,16H,Ar), 3.13 (br, 4H, CH_2-Thiophen), 0.25-2.25(br,1126 H). ^{19}FNMR ($CDCl_3$) δ:-110.17 (s), 115.34 (s). Anal. Calcd for $C_{116}H_{150}F_4N_4S_5$, %: C,75.85; H, 8.23; N,3.05; F,4.14, S,8.73. Found, %: C,75.46; H, 8.17; N, 2.85; F, 3.84, S, 8.43.

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2. M.L. Keshtov, S.A. Kuklin, N. A. Radychev, I. E. Ostapov, A. Yu. Nikolaev, I. O. Konstantinov, M. M. Krayushkin, E. N. Koukaras, A. Sharma and G. D. Sharma,*RSC Adv.*, *2016, 6, 71232–71244*
3. M. L. Keshtov, I. O. Konstantinov, M. M. Krayushkin, S. A. Kuklin, S. M. Masoud,S. N. Osipov, and A. R. Khokhlov, Doklady Chemistry, 2016, Vol. 468, Part 2, pp. 202–207
4. Peng Liu, Kai Zhang, Feng Liu, Yaocheng Jin, Shengjian Liu, Thomas P. Russell, Hin-Lap Yip, Fei Huang, and Yong Cao. Chem. Mater. 2014, 26, 3009−3017

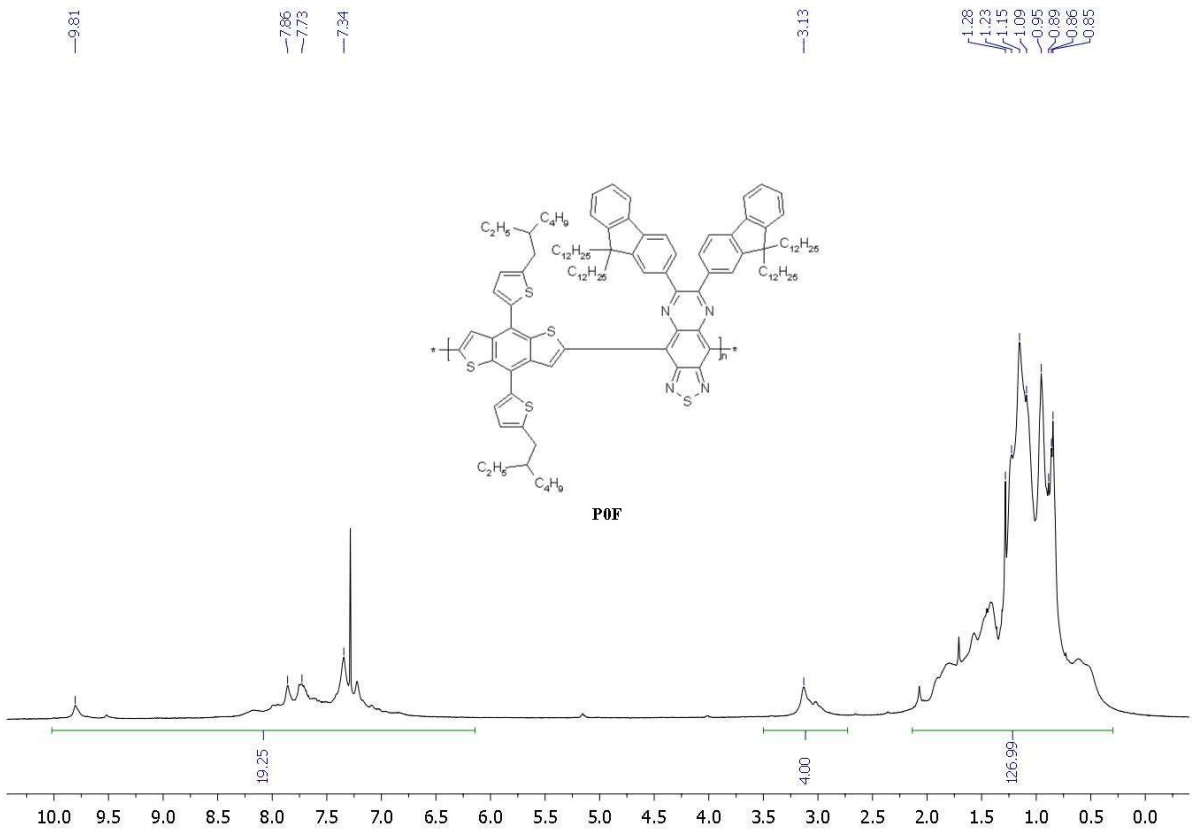

Figure S1 [1]HNMR spectra of copolymer **P0F**

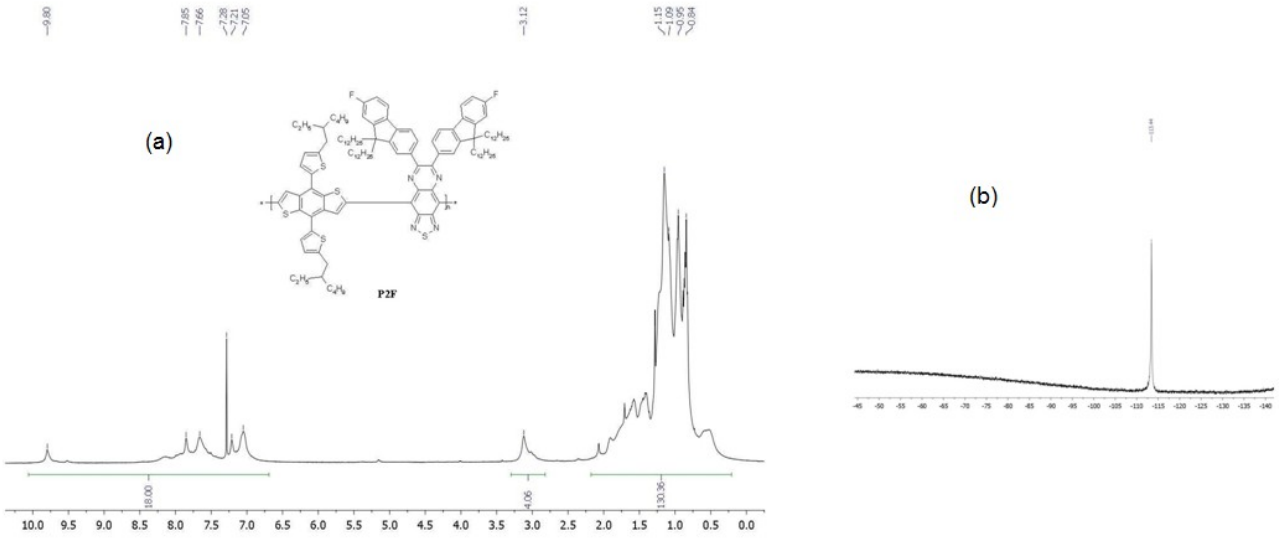

Figure S2 [1]HNMR(a) and [19]F NMR(b) spectra of copolymer **P2F**

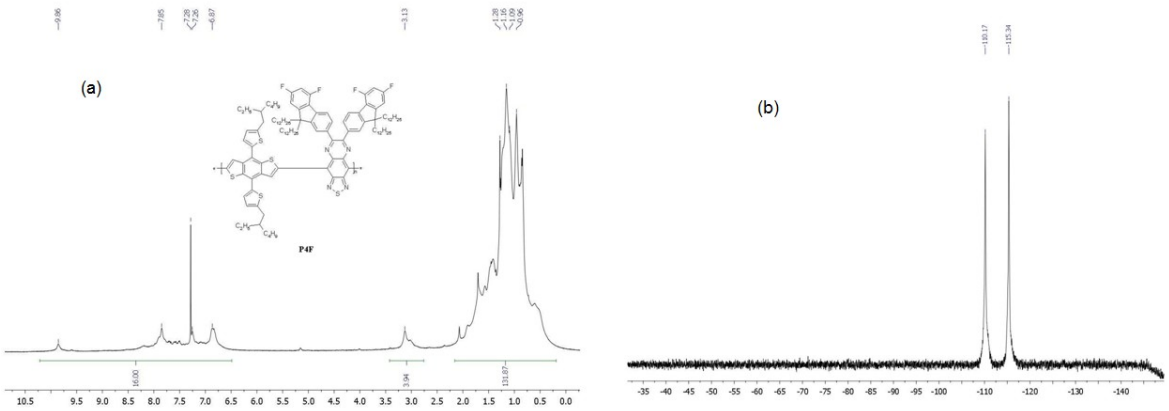

Figure S3 ^{1}HNMR(a) and ^{19}F NMR(b) spectra of copolymer **P4F**

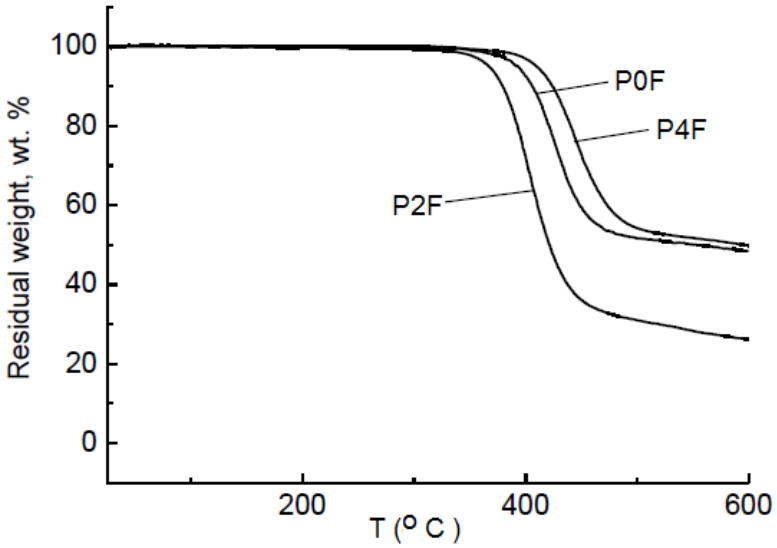

Figure S4 TGA of the copolymers **P0F**, **P2F** and **P4F** with a heating rate of 10 °C/min under an inert atmosphere.

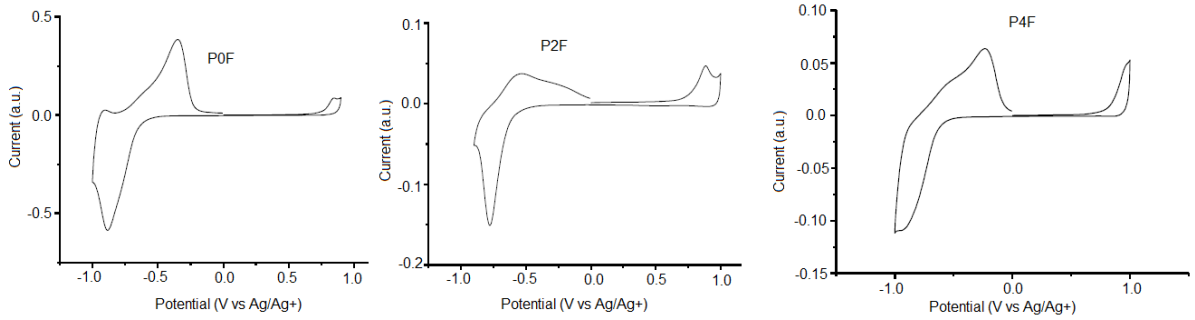

Figure S5 Cyclic voltammograms of copolymers **P0F**, **P2F** and **P4F** in acetonitrile-$[Bu_4N]Cl0_4$ at a scan rate 100 mVs^{-1}